PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-005759

(43)Date of publication of application : 10.01.1997

(51)Int.Cl. G02F 1/1339
C09J 4/00
G02F 1/13

(21)Application number : 07-156200

(22)Date of filing : 22.06.1995

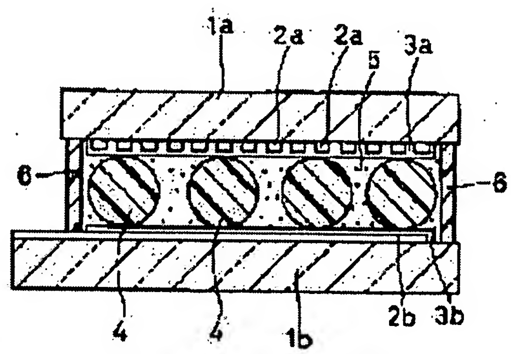
(71)Applicant : MATSUSHITA ELECTRIC IND CO LTD

(72)Inventor : YAMADA SATOSHI
MATSUKAWA HIDEKI

(54) LIQUID CRYSTAL SEALING MATERIAL AND LIQUID CRYSTAL DISPLAY DEVICE

(57)Abstract:

PURPOSE: To provide such a liquid crystal sealing material for a liquid crystal panel that shows little shrinkage during hardening and thermal expansion, has excellent adhesion property and moisture resistance and that radical polymn. is not prevented during hardening with UV rays, and to provide a liquid crystal display device using this sealing material and having good display quality and high reliability against the environment.



CONSTITUTION: A liquid crystal 5 is sealed in the space between two substrates 1a, 1b each having an electrode 2a, 2b and an orienting film 3a, 3b, respectively, with a sealing material 6 to obtain a liquid crystal display device. The sealing material to adhere the two substrates and to seal the liquid crystal consists of 68wt.% bisphenol-A epoxy acrylate oligomer, 5wt.% pentaerythritol, 5wt.% ethoxydiethylene glycol acrylate, 5wt.% 2,2-dimethoxy-2phenylacetone as a photopolymn. initiator, 4wt.% modified aromatic amine-based thermosetting agent, 3wt.% γ-glycidoxypropyl trimethoxy silane, 10wt.% magnesium silicate hydrate, and 3wt.% silicon dioxide. This sealing material is hardened by irradiation of UV rays and heat.

LEGAL STATUS

[Date of request for examination]	29.07.1996
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	2846842
[Date of registration]	30.10.1998
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

English translation of Publication 1

JP-A-9-5759

(54) [Title of the Invention] Liquid crystal sealing material and liquid crystal display device

(57) [Abstract]

[Purpose] To provide a liquid crystal sealing material for use in a liquid crystal panel with less cure shrinkage and heat expansion, not hindered for radical polymerization upon UV-ray curing and excellent in adhesion and moisture resistance, as well as a liquid crystal display device of good display quality and high environmental reliability using the same.

[Constitution] It relates to a liquid crystal display device in which liquid crystals 5 are sealed with a sealing material 6 in a gap between two substrates (1a, 1b) having electrodes (2a, 2b) and orientation films (3a, 3b) in which two substrates are adhered, and a sealing material comprising 68 wt% of bisphenol A type epoxy acrylate oligomer, 5 wt% of pentaerythritol, 5 wt% of a ethoxydiethylene glycol acrylate, 5 wt% of a photoinitiator: 2,2-dimethoxy-2-phenyl acetone, 4 wt% of a modified aromatic amine type heat-curing agent, 3 wt% of γ-glycidoxy propyl trimethoxy silane, 10 wt% of hydrous magnesium silicate and 3 wt% of silicon dioxide is used as the sealing material for sealing liquid crystals and heat set by irradiation of UV-rays.

[Scope of the Claim for Patent]

[Claim 1]

A liquid crystal sealing material for use in a liquid crystal display panel containing a UV-curable ingredient and a thermosetting ingredient in which the ingredient contains an epoxy(meth)acrylate, a (meth)acrylate ester, a photoinitiator, a heat-curing agent, a silane coupling agent, and an inorganic filler as an essential ingredient, and the (meth)acrylate ester contains from 5 to 10% by weight of the (meth)acrylic ester having a plurality of (meth)acrylic acid residues in one molecule in the sealing material, and from 2 to 10% by weight of the (meth)acrylate ester having one (meth)acrylic acid residue in one molecule in the sealing material.

[Claim 2]

A liquid crystal sealing material for use in a liquid crystal display panel according to claim 1, wherein the epoxy(meth)acrylate is a bisphenol A or novolac type epoxy(meth)acrylate and contained within a range from 40 to 70% by weight in the liquid crystal sealing material.

[Claim 3]

A liquid crystal sealing material for use in a liquid crystal display panel according to Claim 1 or 2 wherein the photoinitiator is a photoinitiator selected from the group consisting of acetophenone type photoinitiators, benzoin type photoinitiators, and benzophenone type photoinitiators, and contained within a range from 3 to 5% by weight in the liquid

crystal sealing material.

[Claim 4]

A liquid crystal sealing material for use in a liquid crystal display panel according to any one of claims 1 to 3,wherein the heat-curing agent is a heat-curing agent selected from the group consisting of hydrazides, aromatic amines, acid anhydrides and imidazoles and is contained within a range from 2 to 5% by weight in the liquid crystal sealing material.

[Claim 5]

A liquid crystal sealing material for use in a liquid crystal display panel according to any one of claims 1 to 4,wherein the heat-curing agent is a solid particulate heat-curing agent with an average grain size of 3 μm or less.

[Claim 6]

A liquid crystal sealing material for use in a liquid crystal display panel according to any one of claims 1 to 5, the silane coupling agent is a silane coupling agent selected from the group consisting of glycidyl ethoxy silane and glycidyl methoxy silane, and contained within a range from 2 to 7% by weight in the liquid crystal sealing material.

[Claim 7]

A liquid crystal sealing material for use in a liquid crystal display panel according to any one of claims 1 to 6, wherein the inorganic filler is an inorganic filler of an average grain size of 1.5 μm or less selected from the group consisting of hydrous magnesium silicate, calcium carbonate,

aluminum oxide, and silica and contained within a range from 8 to 20% by weight in the liquid crystal sealing material.

[Claim 8]

A liquid crystal sealing material for use in a liquid crystal display panel according to any one of claims 1 to 7, wherein the liquid crystal display panel is manufactured by steps including a step of dropping and injecting liquid crystals between a step of forming the liquid crystal sealing material and a step of bonding two electrode-attached substrates.

[Claim 9]

A liquid crystal display device having a liquid crystal display panel in which liquid crystals are sealed by the liquid crystal sealing material for use in the liquid crystal display panel as described in any one of claims 1 to 7.

[Claim 10]

A liquid crystal display device according to claim 9, wherein the liquid crystal display panel is manufactured by steps including a step of dropping and injecting liquid crystals between a step of forming the sealing material and a step of bonding two electrode-attached substrates.

[Detailed Description of the Invention]

[0001]

[Industrial Field of Use]

The present invention concerns a liquid crystal sealing material for use in a liquid crystal display panel of a liquid crystal display device usable as a display device for various

electronic equipments, as well as a liquid crystal display device having a liquid crystal display panel sealed by the liquid crystal sealing material.

[0002]

[Prior Art]

For a liquid crystal display device having a liquid crystal display panel in which liquid crystals are sealed in a gap between two substrates having transparent electrodes and applied with orientation treatment, a heat setting one-component type epoxy resin ("STRUCTBOND XN-21-F", manufactured by Mitsui Toatsu Chemical Industry Co.) has been well known as a liquid crystal sealing material used for adhering two substrates and sealing liquid crystals (hereinafter simply referred to as a sealing material).

[0003]

The sealing material comprising a heat setting epoxy resin as an ingredient involves problems such that the viscosity of sealing material is lowered upon curing to cause lateral positional displacement between two substrates which are previously positioned and bonded to each other, that is, misalignment of the substrates, warp is caused to the substrates since the temperature necessary for curing is as high as about 150°C, or curing time is long, etc. to result in lowering of the yield, lowering of the operation efficiency, and lowering of the display quality of the liquid crystal display device.

[0004]

For solving such problems, there is a method of using a UV-curable sealing material or a sealing material comprising a combination of UV-curable ingredient and a thermosetting ingredient. At first, the UV-curable sealing material generally includes those containing (meth)acrylic acid type monomers having a curing mechanism by radical polymerization ["(meth)acrylic ---" means "acrylic ---" and/or "methacrylic ---", which is used in the same meaning also in the invention]. However, since the cure shrinkage during UV-curing is large in the radical polymerization, it results in a significant problem in the adhesion property and the moisture resistance of a liquid crystal panel. For preventing such cure shrinkage, it has also been proposed to use a modified urethane acrylate in JP-A Nos. 7-13173 and No. 7-13174.

[0005]

Then, for the sealing material of using the UV-curable ingredient and the thermosetting ingredient in combination, commercial products (for example, "WORLD LOCK X-8700", manufactured by Kyoritsu Chemical & Co., Ltd.) or JP-A No. 7-13175, etc. using the (meth)acrylic acid monomer for the UV-curable ingredient and using an epoxy resin for the thermosetting ingredient have been known.

[0006]

Further, in the liquid crystal panel manufactured by a dropping method of providing a step of dropping and injecting a liquid crystal between a step of forming a sealing material to an electrode-attached substrate applied with an

orientation treatment and a step of bonding opposed substrates by way of spacer means, since the uncured sealing material and liquid crystals are in contact with each other, it needs a sealing material capable of UV-ray curing that is polymerized by the radical polymerization mechanism. In a case of using a monomer or an oligomer that is polymerized by the cationic polymerization mechanism, since cationic type is used as the photoinitiator for the sealing material, it results in a problem of leaching ion ingredients into liquid crystals to cause orientation failure of the liquid crystals, increase of the current value, etc. In view of the above, a double sealing method of using a UV-curable sealing material that is polymerizated by the radical polymerization mechanism on the side in contact with the liquid crystals and using an epoxy type sealing material at the periphery thereof is proposed in JP-A No. S62-89025.

[0007]

[Subject to be Solved by the Invention]

For the UV-curable sealing material described above, in a case of using a resin formed from (meth)acrylic acid type monomers having the curing mechanism by radical polymerization, since cure shrinkage during cure is large, it results in a problem such as poor adhesion property or moisture resistance of the liquid crystal panel. For solving such problems, there has been known, as proposed in JP-A Nos.7-13173 and 7-13174, a method of preventing cure shrinkage by incorporation of urethane acrylate thereby improving

adhesion with the substrate and improving the adhesion property and the moisture resistance. However, urethane acrylate causes heat expansion and is poor in the heat resistant. Particularly, in the annealing step conducted for making the indication uniform in the plane of the liquid crystal display device, since the annealing is applied at a temperature higher than the nematic-isotropic phase transition temperature of the liquid crystal (usually 80°C to 120°C), expansion of the sealing material containing the urethane acrylate occurs to result in a problem that unevenness in the threshold voltage is caused depending on the gap height at the periphery of the liquid crystal panel seal portion of a liquid crystal display device having such a liquid crystal panel.

[0008]

Further, for the sealing material of using a UV-curable ingredient and a thermosetting ingredient in combination, since the UV-curable ingredient uses a resin polymerized from (meth)acrylic acid type monomers and the thermosetting ingredient uses the epoxy resin, the epoxy resin hinders the radical polymerization of the (meth)acrylate acid monomers upon UV-ray curing to require a large amount of UV-ray energy for obtaining sufficient polymerization. Further, since the thermosetting ingredient is the epoxy resin, it needs heat setting at high temperature for long time to result in a worry of lowering the yield due to the problems such as warping of glass substrates in view of the production.

[0009]

Further, in the dropping method described above, the double sealing method is adopted. However, in the double sealing method, twice or more seal width is required than usual and the area that can be used substantially as a display part of a liquid crystal panel is narrowed, and this provides a great limit with a view point of the product design for the liquid crystal panel. In a case of using the sealing material of a type using the UV-curable ingredient and the thermosetting ingredient together, since the epoxy resin as the thermosetting ingredient hinders the radical polymerization by UV-rays of the (meth)acrylic acid monomer, polymerization does not proceed sufficiently, so that unreacted epoxy resin leaches into the liquid crystals upon subsequent heat setting, to bring about failure in the orientation of liquid crystals.

[0010]

The invention intends to solve the problems in the sealing material described above by incorporating only the (meth)acrylic type monomer or oligomer that is polymerized by the radical polymerization mechanism to the sealing material of a type using the UV-curable ingredient and thermosetting ingredient in combination as the monomer or the oligomer ingredient thereof to be polymerized, and provide a liquid crystal sealing material for use in a liquid crystal display panel of a liquid crystal display device excellent in the adhesion property and the moisture resistance of the liquid

crystal panel, not hindered for the radical polymerization upon UV-ray curing, requiring no heat setting at high temperature for long time, free from drawbacks of causing orientation failure in liquid crystals and also usable for the dropping method, as well as a liquid crystal display device of improved display quality and reliability having a liquid crystal display panel sealed by the liquid crystal sealing material described above.

[0011]

[Means for the Solution of the Subject]

For solving the foregoing subject, a liquid crystal sealing material for use in a liquid crystal display panel according to the invention provides a liquid crystal sealing material containing a UV-curable ingredient and a thermosetting ingredient in which the ingredient contains epoxy(meth)acrylate, a (meth)acrylate ester, a photoinitiator, a heat-curing agent, a silane coupling agent, and an inorganic filler as an essential ingredient, and the (meth)acrylate ester contains from 5 to 10% by weight of the (meth)acrylic ester having a plurality of (meth)acrylic acid residues in one molecule, and from 2 to 10% by weight of the (meth)acrylate ester having one (meth)acrylic acid residue in one molecule in the sealing material.

[0012]

In the liquid crystal sealing material of the invention, it is preferred that the epoxy(meth)acrylate is bisphenol A or novolac type epoxy(meth)acrylate and the

epoxy(meth)acrylate is contained within a range from 40 to 70% by weight in the liquid crystal sealing material.

[0013]

Further, in the liquid crystal sealing material of the invention, it is preferred that the photoinitiator is a photoinitiator selected from the group consisting of acetophenone type photoinitiators, benzoin type photoinitiators, and benzophenone type photoinitiators, and the photoinitiator is contained within a range from 3 to 5% by weight in the liquid crystal sealing material.

[0014]

Further, in the liquid crystal sealing material of the invention, it is preferred that the heat-curing agent is a heat-curing agent selected from the group consisting of hydrazides, aromatic amines, acid anhydrides, and imidazoles and the heat-curing agent is contained within a range from 2 to 5% by weight in the liquid crystal sealing material.

[0015]

Further, in the liquid crystal sealing material of the invention, it is preferred that the heat-curing agent is a solid particulate heat-curing agent with an average grain size of 3 μm or less. Further, in the liquid crystal sealing material of the invention, it is preferred that the silane coupling agent is a silane coupling agent selected from the group consisting of glycidyl ethoxy silane and glycidyl methoxy silane, and the silane coupling agent is contained in a range from 2 to 7% by weight in the liquid crystal sealing

material.

[0016]

Further, in the liquid crystal sealing material of the invention, it is preferred that the inorganic filler is an inorganic filler of an average grain size of 1.5 μm or less selected from the group consisting of hydrous magnesium silicate, calcium carbonate, aluminum oxide, and silica, and the inorganic filler is contained within a range from 8 to 20% by weight in the liquid crystal sealing material.

[0017]

Further, the liquid crystal sealing material of the invention is extremely suitable as a liquid crystal sealing material for use in a liquid crystal display panel manufactured by steps including a step of dropping and injecting liquid crystals between a step of forming the liquid crystal sealing material and a step of bonding two electrode-attached substrates.

[0018]

Further, the liquid crystal display device of the invention is a liquid crystal display device wherein liquid crystals are sealed by the liquid crystal sealing material for use in the liquid crystal display panel as described in any one of the foregoings.

[0019]

In the liquid crystal display device of the invention, the liquid crystal display panel is preferably a liquid crystal display panel manufactured by steps including a step

of dropping and injecting liquid crystals between the step of forming the sealing material and the step of bonding two electrode-attached substrates.

[0020]

[Function]

The liquid crystal sealing material according to the invention uses a combination of the epoxy(meth)acrylate, the (meth)acrylate ester and the photoinitiator that conduct radical polymerization by UV-rays as the UV-curable ingredient, and the heat-curing agent for crosslinking the resin ingredient formed through the radical plymerization by UV-ray irradiation for the UV-curable ingredient as the thermosetting ingredient. As described above, since the epoxy resin is not contained, it is not necessary to cure the epoxy resin by heating for long time and, since the viscosity of the sealing material is not lowered by heating, there is no worry of misaligned of the bonded substrates or the warp of the substrate, and the cure shrinkage can be suppressed. Further, there is no worry that the radical polymerization of the epoxy(meth)acrylate and the (meth)acrylate ester is hindered by the presence of the epoxy resin during UV-ray curing. Further, it is unlikely for unreacted epoxy resin to elute into the liquid crystals upon heat curing to cause orientation failure of the liquid crystals, and a sealing material capable of attaining a liquid crystal panel of excellent adhesion property and moisture resistance can be provided. Accordingly, the liquid crystal display device

having a liquid crystal panel in which the liquid crystals are sealed with the sealing material of the invention can provide a liquid crystal display device of good display quality and good reliability having a liquid crystal panel without orientation failure of the liquid crystals and increase of current value, and excellent in the adhesion property and the moisture resistance. As described above, since the sealing material used in the invention can prepare a liquid crystal panel of excellent adhesion property and moisture resistance while utilizing the curing mechanism by radical polymerization, a liquid crystal display device of high display quality and reliability can be provided.

[0021]

Further, since the sealing material of the invention has the curing mechanism by the radical polymerization, the reaction rate during UV-ray curing is high and, also in a case of adopting the dropping method including a step of dropping and injecting the liquid crystals between the step of forming the sealing material on one of two electrode-attached substrates applied with the orientation treatment and bonding the two substrates by way of other substrate and the spacer means, this does not give significant effects on the orientation state and the electric characteristic of the liquid crystals. Particularly, also in the heat setting of the sealing material conducted after UV-ray curing, the efficiency of the productivity is not deteriorated by properly selecting a heat-curing agent capable of polymerization at an

annealing temperature of the liquid crystal panel or lower. Accordingly, a liquid crystal display device of good display quality can be provided efficiently also in the dropping method.

[0022]

In the ingredient of the sealing material according to the invention, since the epoxy(meth)acrylate ingredient has relatively low heat expansion and polymerization proceeds rapidly therein, this is an effective ingredient for preventing leaching of the ingredient in the uncured sealing material into the liquid crystals by the contact of the sealing material and the liquid crystals that results in orientation failure of the liquid crystals or increase of the current value of the obtained liquid crystal display device also in a case of using a so-called dropping method of providing a step of dropping and injecting liquid crystals between the step of forming the sealing material to the electrode-attached substrate applied with the orientation treatment and a step of bonding the opposing substrates by way of and spacer means. The epoxy(meth)acrylate ingredient is usually available in the form of an oligomer and is used as an ingredient of the starting material of the invention in the form of the oligomer.

[0023]

The (meth)acrylate ester having plural (meth)acrylic acid residues in one molecule has a useful role of increasing the cure density, promoting heat setting to attain a seal of high temperature reliability. In a case where the ingredient

is less than 5% by weight in the sealing material, the crosslinking density becomes insufficient failing to obtain a liquid crystal display device of high heat reliability. Further, in a case where it exceeds 10% by weight, it is not preferred since cure shrinkage tends to be formed.

[0024]

Further, the (meth)acrylate ester having one (meth)acrylic acid residue in one molecule is useful as an ingredient with relatively less cure shrinkage and suppressing cure shrinkage and has a role of a solvent such as for the epoxy(meth)acrylate ingredient in the stage of the monomer before polymerization and, accordingly, can play a role capable of controlling to an appropriate viscosity upon coating the sealing material by printing or the like on the substrate as a viscosity controller. In a case where the ingredient is less than 2% by weight in the sealing material, cure shrinkage of the sealing material tends to be caused. On the other hand, in a case where it is more than 10% by weight, the crosslinking density is lowered to deteriorate the heat reliability of the obtained liquid crystal display device, as well as the uncured ingredient leaches into the liquid crystals due to the excessive amount to result in a problem such as orientation failure of the liquid crystals.

[0025]

The photoinitiator has a role of a radical source necessary for UV-ray polymerization of various (meth)acrylic monomers or oligomers. The heat-curing agent mainly

contributes to the heat crosslinking and heat setting of the polymer ingredient formed by the UV-ray polymerization and has a role of attaining the improvement in the adhesion property and the improvement in the heat reliability.

[0026]

Further, the silane coupling agent is an effective ingredient of further improving the moisture resistance, and the inorganic filler is an ingredient contributing to the adhesion property such as improvement of the peeling strength and also serves to the control of the viscosity of the sealing material.

[0027]

Since the sealing material of the invention uses the ingredients as described above, it is excellent in the adhesion property and the moisture resistance and has high display quality and reliability while it utilizes the curing mechanism by radical polymerization. Then, referring further to preferred embodiments of the invention, it is preferred that the epoxy(meth)acrylate is a bisphenol A or novolac type epoxy(meth)acrylate and contained within a range from 40 to 70% by weight in the liquid crystal sealing material. The bisphenol A type or novolac type epoxy(meth)acrylate is preferred having a viscosity which can be controlled to an appropriate range of viscosity upon coating the sealing agent by printing, causing less heat expansion compared with the modified urethane acrylate or the like. Further, it is preferred to define the ratio of use within a range from 40

resistance. Further, in a case where the blending ratio of the silane coupling agent is excessively small, it scarcely contributes to the further improvement of moisture resistance of the liquid crystal panel. In a case where it is excessive, it may intrude into the liquid crystals to possibly cause orientation failure. In a case where the agent is contained in the liquid crystal sealing material within a range from 2 to 7% by weight, it is preferred since such problems need not be considered at all.

[0032]

Further, the inorganic filler is preferably defined as an inorganic filler selected from the group consisting of hydrous magnesium silicate, calcium carbonate, aluminum oxide, and silica in view of the reason that those of an average grain size of 1.5 μm or less are relatively available easily, the effect of improving the adhesion property is greater, and viscosity of the sealing material can be controlled easily in a case of coating the sealing material by printing. Further, the inorganic filler preferably has the average grain size of 1.5 μm or less since the dispersibility in the sealing material is favorable and, in addition, since the average grain size is smaller than the gap of two substrates of the liquid crystal panel to be controlled by the spacer, etc., it gives no undesired effects on the gap of the two substrates of the liquid crystal panel. While the lower limit of the average grain size of the inorganic filler is not particularly restricted, those of a small size usually of about 15 nm can

be used suitably. In a case where the blending ratio of the inorganic filler is excessively small, further improving effect for the adhesion property is not sufficient. In a case where it is excessive, since it is not appropriate in a case of forming the sealing material by coating on the substrate by printing or the like and it becomes difficult to keep a predetermined distance for the gap between the two substrates. It is preferably contained within a range from 8 to 20% by weight in the liquid crystal sealing material since it is not necessary at all to consider such problems.

[0033]

Further, by controlling the blending amount of the (meth)acrylate ester containing one or more (meth)acrylic acid residues in one molecule, and the blending amount of the inorganic filler within the range for the blending amount, a viscosity of the sealing material suitable to the printability and the adjustment for alignment after bonding can be obtained and the liquid crystal display device can be produced efficiently.

[0034]

In addition, by defining the grain size of the inorganic filler to 1.5 μm or less, since the thixotropy of the sealing material can be improved, there is no problems such as degradation of the orientation due to sagging of the sealing material and breakage of the sealing material after bonding the substrates in the dropping method, and a liquid crystal display device of good display quality can be provided.

[0035]

[Example]

In the liquid crystal display device of the invention, since the sealing material used is a type of using in combination the UV-curable ingredient and the thermosetting ingredient having the radical polymerization mechanism, those of high reliability and display quality can be obtained. For the liquid crystal display devices per se of the invention, since those of constitutions known so far can be adopted except for the composition of the sealing material, detailed descriptions therefor are to be omitted.

[0036]

Specific examples for each of the ingredients of the sealing material are to be described. As the epoxy(meth)acrylate, the bisphenol A or novolac type epoxy (meth)acrylate is preferred, and specific examples of the bisphenol A type epoxy(meth)acrylate include bisphenol A type glycidyl ether modified diacrylate, and specific examples of the novolac type epoxy(meth)acrylate include a novolac type glycidyl ether modified diacrylate. In the example, "SP-1563" as a bisphenol A type epoxy acrylate oligomer manufactured by Showa High Polymer Co., Ltd. was used.

[0037]

Among the (meth)acrylate esters, specific examples of the (meth)acrylate ester having plural (meth)acrylic acid residues in one molecule include pentaerythritol triacrylate and pentaerythritol tetraacrylate and, in the example,

pentaerythritol triacrylate, "Biscoat #300", manufactured by Osake Organic Chemical Industry Ltd. was used.

[0038]

Among the (meth)acrylate esters, specific examples of the (meth)acrylate esters having one (meth)acrylic acid residue in one molecule include tetrahydrofulfryl acrylate, 2-hydroxypropyl acrylate, and ethoxydiethylene glycol acrylate and, in the example, ethoxydiethylene glycol acrylate, "EC-A", manufactured by Kyoei Kagaku Kogyo Co. was used.

[0039]

As the photoinitiator, the acetophenone type photoinitiator, the benzoin type photoinitiator, and the benzophenone type photoinitiator are preferred and specific examples of the acetophenone type photoinitiator include diethoxy acetophenone, 4-t-butyl-dicycloacetophenone, and 2,2-dimethoxy-2-phenylacetone, and specific examples of the benzoin photoinitiator include benzoin, benzoin ethyl ether, and benzyl methyl ketal, and specific examples of the benzophenone type photoinitiator include benzophenon, 4-phenyl benzophenone, and hydroxy benzophenone and, in the example, 2,2-dimethoxy-2-phenylacetone, "Ilugacure 651", manufactured by Nippon Ciba Geigy Co. was used.

[0040]

As the heat-curing agent, hydrazide type, aromatic amine type, acid anhydride type, and imidazole type are preferred, and specific examples of the hydrazide type heat-curing agent

include 7,11-octadecadienedihydrazide and dihydrazide adipate, specific examples of the aromatic amine type heat-curing agent include diaminodiphenyl methane and methaphenylene diamine, specific examples of the acid anhydride type heat-curing agent include hexahydrophthalic acid anhydride, and tetrahydrophthalic acid anhydride and specific examples of the imidazole type heat-curing agent include 2-ethylmethyl imidazole, 2-methyl imidazole, 1-benzyl-2-methyl imidazole, etc. In the example, "UDH" manufactured by Ajinomoto Co. Inc., as the hydrazide type solid granular heat-curing agent (controlled to average grain size 3 μm by three rolls), or flaky "Epicure Z" manufactured by Yuka Shell Epoxy Co. as the modified aromatic amine was used.

[0041]

As the silane coupling agent, glycidyl ethoxysilane and glycidyl methoxysilane were used preferably and, in the example, γ-glycydoxy propyl trimethoxy silane, "KBM 403", manufactured by Shin-Etsu Chemical Co., Ltd. was used.

[0042]

As the inorganic filler, hydrous magnesium silicate, calcium carbonate, aluminum oxide, and silica were used preferably and, in the example, hydrous magnesium silicate, "Super talc SG-95" (average grain size: 1.4 μm), manufactured by Nippon Talc Co., Ltd. and silicon dioxide, "Aerosil R202", manufactured by Nippon Aerosil Co., Ltd. (average primary grain size: 15 nm) were adopted.

[0043]

For the curing condition, a usual high pressure mercury lamp was used for the UV-ray curing and the irradiation conditions are different depending on the kinds of lamps to he used, composition and the amount of the sealing material, and the distance from the lamps, etc. and they may be controlled properly in accordance with the conditions. While not particularly restricted, an irradiation condition, for example, about from 600 mJ to 5000 mJ is adopted in view of the energy amount. In the example, "HGQ-2000" manufactured by Nippon Denchi Co. as the high pressure mercury lamp was used and UV-rays at a wavelength of 420 nm or less was irradiated at illuminance of UV-rays of 20 mW/cm^2 for 2 min to the sealing material such that the irradiation energy was 4800 mJ. Also for the heat setting, conditions are different depending on the kinds of the heat-curing agent used, kinds of other materials, blending ratio, etc. and are not particularly restricted. For example, a condition about at 100 to 150°C for one hour or more is usually adopted and, in the example, irradiation was conducted at 120°C for 12 hours, which was equal with the annealing condition of the liquid crystal panel.

[0044]

While the invention is to be described further with reference to specific examples and comparative examples, the invention is not restricted only to those described in the examples.

(Examples 1 to 3, Comparative Examples 1 to 3)

An example and a comparative example of liquid crystal display devices using sealing materials according to the invention and comparative examples are to be described. Fig. 1 is a schematic cross sectional view of a liquid crystal panel used for evaluation in this case. A glass substrate 1a is provided at the inner surface thereof with a transparent electrode 2a formed of ITO (oxide indium and tin) and an oriented polyimide orientation film 3a further inner surface thereof, and a glass substrate 1b is provided at the inner surface thereof with a transparent electrode 2b formed of ITO (oxide indium and tin) and an oriented polyimide orientation film 3b further inner surface thereof. For the two electrode-attached glass substrates 1a and 1b applied with the orientation treatment, a cell gap is controlled by a resin bead spacer material 4 (particle size 7.4 μm) arranged at a predetermined density by scattering, the two electrode-attached substrates are bonded by a sealing material 6 and liquid crystals 5 are sealed therein. The sealing material 6 is disposed in a region outside to the region where polyimide orientation films 3a, 3b are disposed for controlling orientation so as not to overlap the region disposed with the polyimide orientation films 3a, 3b. In Examples 1 to 3 and Comparative Examples 1 to 3, liquid crystal panels are assembled previously and the liquid crystals 5 are injected subsequently.

[0045]

Table 1 below shows each of the ingredients and the blending amount thereof of the sealing materials, the adhesion property at the initial state and 8 hours after a pressure cooker test at 120°C, 120%, 2 atm (hereinafter simply referred to as PCT), the orientation state and the change of current value of the liquid crystals of liquid crystal display devices 1000 hours after a high temperature test at 120°C, and the orientation state of the liquid crystals and the change of the current value of the liquid crystal display devices 1,000 hours after a moisture resistance test at 60°C 95% for Examples 1, 2, and 3 and Comparative Examples 1, 2, and 3.

[0046]

[Table 1]

		Example			Comparative Example		
		1	2	3	1	2	3
"SP-1563"		65	60	65	50	70	65
"Biscoat #300"		5	10	5	5	5	7
"EC-A"		5	5	5	20		7
"KBM403"		3	3	3	3	3	3
"Ilugacure 651"		5	5	5	5	5	5
"Epicure Z"		4	4		4	4	
"UDH"				4			
"Super talc SG-95"		10	10	10	10	10	10
"Aerosil R202"		3	3	3	3	3	3
Adhesion property	Initial	⊙	⊙	⊙	⊙	X	Δ
	PCT: 8 hrs	⊙	⊙	⊙	⊙	X	X
Current value	120°C, 1000 hrs.	⊙	⊙	⊙	Δ	⊙	O
	60°C, 95%, 1000hrs.	⊙	⊙	⊙	X	⊙	X
Orientation state	120°C, 1000 hrs.	⊙	⊙	⊙	X	⊙	⊙
	60°C, 95%, 1000 hrs.	⊙	⊙	⊙	X	⊙	⊙

⊙: good
O: no problem in use
Δ: problem may be present in future use
X: not usable

[0047]

The evaluation criterion concerns the evaluation whether they are usable or not in usual circumstances where

OA equipments such as personal computers or word processors are used and "The problem may be present in future use" for symbol Δ means that there may be a problem in use under severer conditions, that is, under circumstantial conditions assuming application uses expected to be developed in near future such as the use for automobile mounting or outdoor use.

[0048]

Examples 1 and 2 are different in that the blending amount of "Biscoat #300" as a sort of the (meth)acrylate ester having plural (meth)acrylic acid residues in one molecule are 5% by weight and 10% by weight respectively, and Examples 1 and 3 are different in that the heat-curing agents are modified aromatic amine type "Epicure Z" and hydrazide type "UDH" respectively and are identical for other ingredients and the blending amount for each of the ingredients. In Comparative Example 1, "EC-A" as a sort of the (meth)acrylate ester having one (meth)acrylic acid residue in one molecule is blended excessively as 20% by weight of the blending amount. In Comparative Example 2, "EC-A" is removed and, in Comparative Example 3, the heat-curing agent is removed.

[0049]

In Comparative Example 1, the orientation state of the liquid crystals after leaving at a high temperature is deteriorated. In addition, the current value increases both in the moisture resistance test and the high temperature test, and the display quality of the liquid crystal display device is deteriorated.

[0050]

Then, in Comparative Examples 2 and 3, there are no problems for the panel characteristics after the high temperature test and the moisture resistance test. However, in Comparative Example 2, the adhesion property at the initial stage is poor and, in Comparative Example 3, the adhesion property after PCT is poor compared with others.

[0051]

From the foregoings, it is recognized that Examples 1, 2, and 3 can provide liquid crystal display devices with no problem for the adhesion property, and the reliability for high temperature moisture resistance, having good display quality and good reliability, and it can be recognized that they are good sealing material.

[0052]

(Examples 4 to 6, Comparative Examples 4 to 6)

Then, description is to be made to an example of liquid crystal display devices according to the present invention, in a case of manufacturing a liquid crystal display device by a so-called dropping method of including a step of dropping and injecting liquid crystals between a step of forming a sealing material to one of two electrode-attached substrates applied with an orientation treatment and bonding the two substrates by way of (the other substrate) and the spacer means.

[0053]

At first, the dropping method is described with

reference to Fig. 2 and Fig. 3. Fig. 2 is a schematic perspective view for the step of dropping liquid crystals in a case of manufacturing a liquid crystal panel for use in a liquid crystal display device by the dropping method adopted in this example, and Fig. 3 is an end face view of a schematic cross section for a step of bonding a substrate to which liquid crystals are dropped and an opposed substrate in which a spacer material is disposed.

[0054]

In Fig. 2, a sealing material 11 is formed in a optional patterned shape by using screen printing or the like to a portion of the inner surface of an electrode-attached substrate 10b applied with an orientation treatment (identical with the substrate 1b explained for Fig. 1), and liquid crystals 12 are dropped and arranged for the range surrounded with the sealing material by using a liquid discharge device 13 such as a dispenser. Then, as shown in Fig. 3, resin bead spacer material 14 (grain size: 7.4 μm) is arranged and secured at a uniform in-plane density by scattering to the inner surface of the electrode-attached substrate 10a applied with orientation treatment (identical with substrate 1a explained for Fig. 1) which is opposed to the substrate 10b in which the liquid crystals are disposed. Then, the substrates 10a and 10b are bonded to each other under a reduced pressure in a vacuum chamber 15 adjusted to a reduced pressure of 0.4 to 1 Torr, and the substrates are subsequently pressed by atmospheric pressure to control the gap.

[0055]

Table 2 shows each of the ingredients and the blending amount thereof in Examples 4 to 6 and Comparative Examples 4 to 6, the orientation state upon sealing, change of the current value and the orientation state of liquid crystals after a high temperature test at 120°C for 1,000 hours, and the change of the current value and the orientation state of liquid crystals after 1000 hours moisture resistance test at 60°C, 95%.

[0056]

[Table 2]

		Example			Comparative Example		
		4	5	6	4	5	6
"SP-1563"		68	60	68	62	58	55
"Biscoat #300"		5	5	5	8	15	5
"EC-A"		2	10	2	9	2	9
"Epicoat 802"							10
"KBM403"		3	3	3	3	3	3
"Ilugacure 651"		5	5	5	5	5	5
"Epicure Z"		4	4			4	
"UDH"				4			
"Super talc SG-95"		10	10	10	10	10	10
"Aerosil R202"		3	3	3	3	3	3
Orientation state at seal margin		⊙	⊙	⊙	O	X	X
Current value	120°C, 1000 hrs.	⊙	⊙	⊙	O	⊙	O
	60°C, 95%, 1000hrs.	⊙	⊙	⊙	X	⊙	X
Orientation state	120°C, 1000 hrs.	⊙	⊙	⊙	O	O	O
	60°C, 95%, 1000 hrs.	⊙	⊙	⊙	X	⊙	X

⊙: good
O: no problem in use
Δ: problem may be present in future use
X: not usable

[0057]

In this case, Examples 4 and 5 are different in that the blending amount of "EC-A" as a sort of the (meth)acrylate ester having one (meth)acrylic acid residue in one molecule are 2% by weight and 10% by weight respectively, and Examples 4 and 6 are different in that the heat-curing agents are modified

aromatic amine type "Epicure Z" and hydrazide type "UDH" respectively and are identical for the blending amount of each of the ingredients. In Comparative Example 4, "Epicure Z" as the heat-curing agent is not blended. In Comparative Example 5, "Biscoat #300" as a sort of the (meth)acrylate ester having plural (meth)acrylic acid residues in one molecule is blended excessively as 15% by weight. In Comparative Example 6, "Epicoat 802" manufactured by Yuka Shell Epoxy Co. is blended as the epoxy resin, and the heat-curing agent is blended by the epoxy equivalent amount thereof.

[0058]

In view of the result, in Comparative Examples 5 and 6, since the not yet cured ingredients tend to leach easily into the liquid crystals and the region of poor orientation of the liquid crystals at the margin of the seal is wide, it erodes the display area. Further, in Comparative Examples 4 and 6, increase of the current value after the moisture resistance test is observed to show a result of poor reliability. This is considered to be attributable, for example, to that uncured ingredients are leached by the water content or liquid crystals at high temperature since the ingredients having no concerns with polymerization upon UV-ray curing such as epoxy resin are contained in a great amount and that the crosslinking density is lowered since the heat-curing agent is not present and, as a result, the moisture permeability increases to lower the moisture resistance.

[0059]

On the contrary, in Examples 4 to 6, the orientation state at the margin of the seal is also satisfactory and there is no problem also for the reliability for high temperature and moisture resistance. Accordingly, by the use of the sealing material according to the invention, a liquid crystal display device of the invention having high reliability and good display quality also in view of the dropping method can be provided.

[0060]

[Effect of the Invention]

The sealing material of the invention is a sealing material using the ingredient having the radical polymerization mechanism and can provide a liquid crystal sealing material for use in a liquid crystal panel with less cure shrinkage and heat expansion, not hindered for the radical polymerization upon UV-ray curing, with less leaching of uncured ingredients into liquid crystals, and excellent in the adhesion property and the moisture resistance. Further, it can provide a liquid crystal display device of good display quality and high reliability having the liquid crystal display panel sealed by the liquid crystal sealing material described above.

[0061]

Further, since the polymerization proceeds by the radical polymerization mechanism in the sealing material, it is free from problems for the use of the dropping method, in view of misalignment of substrates, and sagging or

disconnection of seal in the sealing material by the combined use of the UV-ray curing and, accordingly, it is possible to improve the productivity and improve the yield when applied to the liquid crystal display device.

[Brief Description of the Drawings]

[Fig. 1] is a schematic cross sectional view of a liquid crystal panel for use in a liquid crystal display device as an example of the invention;

[Fig. 2] is a schematic perspective view for a step of dropping liquid crystals in a case of manufacturing a liquid crystal panel for use in a liquid crystal display device by a dropping method;

[Fig. 3] is an end face view of a schematic cross section for a step of bonding a substrate to which liquid crystals are dropped and an opposed substrate in which a spacer material is disposed in a case of manufacturing a liquid crystal panel for use in a liquid crystal display device by a dropping method.

[Description for References]

1a, 1b substrate

2a, 2b transparent electrode

3a, 3b polyimide orientation film

4 resin bead spacer material

5 liquid crystal

6 sealing material

10a, 10b electrode-attached substrate applied with

orientation treatment

11 sealing material

12 liquid crystal

13 liquid <u>dispensing</u> device

14 resin bead spacer material

15 vacuum vessel